QUARTERLY REPORT NO. 1

on the

POWER SOURCES STUDY

Period: May 11, 1956 to August 31, 1956

Reference: [redacted]

STAT

[redacted]

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I. PURPOSE OF THE STUDY

The purpose of this study is to increase the body of knowledge of potential portable electrical energy sources, as well as to develop two specific new devices. To achieve these ends, there are three portions to the program.

A. The first is a study of the literature, of progress made in the field at other installations and throughout the entire electrical energy-source industry, and of the applicability of known systems to the special requirements of portable, lightweight electrical energy sources.

B. The second portion of the program consists of the development of a thermoelectric generator, capable of wide utility in the field with a minimum of auxiliary equipment.

C. The third portion of the program consists of the development of a gas-activated battery system with the inherent advantages of extremely long shelf-life and great portability.

II. ABSTRACT

The main objective during the quarter ended August 31, 1956, was to begin the study of energy sources and to concentrate, in the laboratory, on the development of a thermoelectric generator. Resumes of reports issued to the Customer in the course of our study program will be found in the section following this abstract. Additional information gleaned by consultation with personnel of the Signal Corps Engineering Laboratories on the subjects of fuel cells, nickel-cadmium cells, solar cells, and some earlier developments in the field of thermoelectric generators is also included.

Results of laboratory work in the field of thermoelectric generators indicate that there is wide variability among heat sources in their ability to supply any thermoelectric device with the 1000 watts postulated in the original design of the generator. [redacted] STAT has STAT agreed to furnish information concerning the actual production of zinc antimonide in a form suitable for thermoelements, and the thermoelements themselves. It is planned to follow [redacted] for the fabrication STAT of the thermogenerator before attempting any modifications or improvements.

III. REPORTS AND CONFERENCES

A. Reports Issued

1. On June 1 and June 6, reports were issued to the Customer concerning press releases on an Army Liaison Group in Western Germany. With headquarters in Frankfurt, the group will engage scientists and technicians for research work of interest to the Army. It is their hope that this group will promote research which is further advanced or which is not available in the United States. This group is organized by the Research and Development Division of the United States Department of the Army, under Lieutenant General Gavin.

2. On June 4, a memorandum was sent to the Customer containing, among other things, the results of calculations concerning the feasibility of using a "lecture bottle" of hydrogen as a fuel source for a fuel cell. This standard small tank, measuring 15 inches long and two inches in diameter, contains two cubic feet of the gas at a pressure of 1600 pounds per square inch. The cost of such a cylinder is $7.00, and refilling with hydrogen costs $1.00.

If one assumes that the conversion of chemical into electrical energy is 100 per cent efficient, the contents of this cylinder would produce 135 ampere-hours of current at a potential approximating one volt. The energy output would therefore be 135 watt-hours, at a cost of 5.2 cents per watt-hour, assuming that the tank would not be refilled. The cost of such a system, far greater than that of a conventional lead-acid storage battery of similar capacity, has the advantage of "infinite" shelf-life and increased portability. A fuel cell, if properly designed, might be activated by opening the valve from the gas tank, and de-activated (with a return to long shelf-life) by closing the valve. Extended shelf-life, light weight (of the order of 5 pounds), and the absence of the necessity for maintenance during storage may combine to offset the high cost of the fuel and the additional expense of the fuel cell itself.

Calculations were made to consider other sources of hydrogen after rejection of lithium hydride and lithium aluminum hydride because of their higher cost than tank hydrogen, as well as the necessity for storing them in moisture- and air-tight containers. The Fisher Scientific Company markets an alloy of 35 per cent sodium and 65 per cent lead under the trade name of "Hydrone". It is less expensive than the tank hydrogen and may be stored and handled more readily than the lithium compounds. Hydrone produces hydrogen by chemical reaction between the sodium in the alloy and water. The material may be fabricated in the form of pellets which could be sealed individually in plastic containers and which could be made to supply a predetermined amount of electrical energy upon immersion in water.

To summarize the advantages of Hydrone over tank hydrogen, it may be said that the fuel cost is 3.6 cents per watt hour, compared to 5.2 cents for the tank gas. Only 0.8 pounds of Hydrone is required to generate as much gas as is contained in a five-pound tank. The volume of this quantity of Hydrone would be one-fourth to one-half that of the tank. Because of the possibility of packaging the alloy in a plastic pellet, it would be possible to eliminate the difficulties involved with as high a pressure gas system as would be needed for handling the tank gas. Leakage problems, therefore, would be eliminated. Finally, since no gas is present during the storage period, hazard from the high pressures obtained in the tank does not exist with Hydrone.

The chief disadvantage of Hydrone, when compared to a tank of gas, lies in the complexity of the equipment and the handling required to use it. Although a gas-generating chamber must be developed, in addition to the need for a water supply and disposal facilities for the sodium hydroxide solution and lead sponge which result from the reaction of hydrone with water, these difficulties may be diminished by the careful design of the equipment.

It was concluded, on the basis of the brief study, that substantial amounts of electrical energy may be produced from a fuel cell drawing its supply from a portable source of gas. The choice between a tank of gas and a water-activated gas generator would have to be made on the basis of other considerations than these which were included in the calculations.

3. On June 1, a memorandum was issued concerning the fact that German thermocouple power-sources had been observed [redacted] STAT These were prepared STAT in the laboratory of Dr. E. Justi under commercial sponsorship. Sufficient power was obtained by using a single thermoelement to support several kilograms by means of an electromagnet which received its power from this thermoelement.

4. On June 4, the Customer was informed that the "Radio Amateur Handbook" published in Moscow last year had given a description of a thermocouple generator (type TGK-3). The device consists of two piles containing a large number of series-connected thermocouples made of "metal-ceramics". Heated by a kerosene lamp which simultaneously provides illumination, the two generators produce two volts each, one at a current of two amperes, and the other at a current of one-half ampere.

5. On July 13, a report was sent to the Customer on the subject of a sun-powered portable radio, manufactured by the Admiral Corporation. The power supply consists of a sun-powered pack containing 32 silicon cells enclosed under a plastic window. This solar supply is priced at $185.00 and may be used in place of the six conventional flashlight batteries normally supplied with the radio.

B. Conferences

1. On August 16 and 17 the staff visited with the Signal Corps Engineering Laboratories at Ft. Monmouth, New Jersey. There, they conferred with members of the Power Sources Division, [redacted] STAT

[redacted] The discussions centered on the general STAT field of power sources, the field of fuel cells, that of conventional electrochemical systems, and solar and thermoelectric sources of electrical energy.

The Signal Corps has sponsored contracts with the University of Minnesota and with the Armour Research Foundation on the general subject of power sources. Both of these studies produced large volumes of reports, but no truly novel suggestions for further research.

In discussion with [redacted] STAT

[redacted] specifications of several practical fuel cells were STAT discussed. They pointed out that the innovation by Dr. Justi was his high-efficiency hydrogen electrode which functions at a relatively low temperature of 80 degrees Centigrade. In addition, the current density of his configuration is higher than has been previously attained. [redacted] STAT both worked in Austria, where they studied the reaction between hydrogen and oxygen in a fuel cell containing highly concentration potassium hydroxide solutions. Voltages approximating one volt at a current density of about ten milliamperes per square centimeter were observed at room temperature. Both men reported that the temperature of the electrolyte increased due to the flow of current, and that polarization effects make application of the fuel cell to high-power needs seem somewhat remote. They nevertheless pointed out that, for relatively small amounts of power such as those with which this study is concerned, it may be possible to develop a fuel cell which will operate at room temperature.

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[redacted] described some of the work he did while in Germany on the nickel-cadmium electrochemical cell. He explained that the chief virtue of the nickel-cadmium cell lies in the complete absence of disastrous effects when it is overcharged. This is a consequence of the unique reactions taking place between the hydrogen and the cadmium in one electrode. [redacted] agreed, however, that nickel-cadmium cells do not have as long a shelf-life as would be desirable for the purposes of this investigation. STAT STAT

The system involving zinc and silver oxide is known to produce a greater amount of electrical energy per unit-weight than does the nickel-cadmium system, but the rechargeability is far inferior to the rechargeability of the latter system.

Discussions with [redacted] concerning the solid-state devices of interest to the Signal Corps yielded the information that their main current efforts lie in the field of solar cells. Previously, they have investigated the feasibility of thermoelectric generators; however, the results of their contracts produced such bulky devices that they could not effectively be used for the applications then in mind. [redacted] agreed that careful design might make a portable thermoelectric generator of greater efficiency and utility. In the course of their investigations, they have found that a suitable junction between constantan and zinc antimonide may be made by a force fit, followed by a metal-spray application of constantan on the end. This technique differs from that described by [redacted] STAT STAT STAT STAT

Other developments in thermoelectric generators at the Signal Corps include the use of atomic-energy sources for heat. This is a development of the Mound Laboratories for the Atomic Energy Commission, where promethium 147 in a highly-concentrated form was used as the source of heat, due to its natural disintegration. The group at Mound Laboratories reported that as much as 500 watt-hours per pound can be produced by the use of conventional thermocouples and polonium 210 as the source. This compares with 50 watt-hours per pound for conventional chemical systems, — an appreciable improvement.

Work sponsored by the Signal Corps has also included studies of Peltier cooling. Research on this phenomenon, a sort of inverse thermoelectric effect, is being carried out currently at the Franklin Institute in Philadelphia under industrial sponsorship.

In conjunction with the Navy, the Signal Corps is sponsoring several efforts to utilize solar energy for conversion to electrical energy. The Hoffman Electrical Corporation, of Evanston, Illinois, produces a device which obtains a conversion efficiency of between five and ten per cent from a silicon solar cell. Research carried on under Signal Corps contracts by RCA at the Princeton Labs involves a study of polycrystalline materials, with the hope of obtaining a five per cent efficiency. Since previous work with polycrystalline materials has only produced efficiencies of conversion approximating one per cent, the staff of the Signal Corps is not highly optimistic of success.

2. From mid-June to mid-August in the course of negotiations with [redacted] STAT
[redacted] a certain amount of "know-how" was imparted by STAT
her. Much of this information is embodied in the next section, Factual Data, in the sub-division devoted to the development of the thermogenerator.

IV. FACTUAL DATA

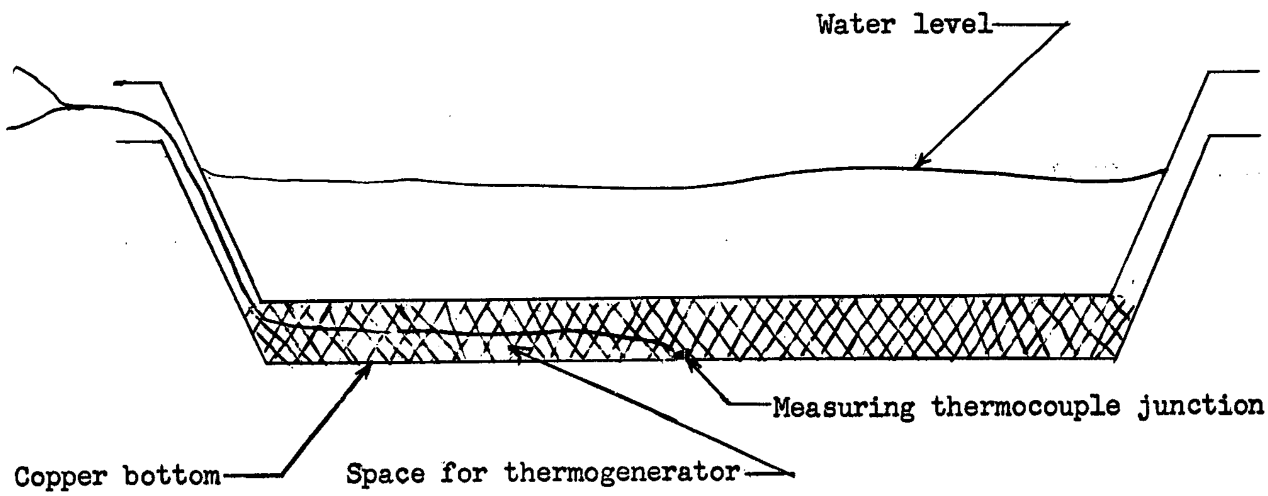
A. Introduction

Since the information gleaned from the study portion of this contract has been reported in memorandum form and in the preceding portion of this report, this section will concern itself mainly with results of laboratory investigations. During this quarter, most of the effort has been devoted toward the production of a thermoelectric generator. The gas-activated battery system has been neglected in order that the ground work for the thermoelectric generator program may be established.

B. Thermoelectric Generator Development

As is shown in the sketch in Figure 1, the thermoelectric generator takes the form of a double-bottomed pan. Placed between the two bottoms of this device (at least in early models) is a series of approximately 200 thermocouples, consisting of zinc antimonide and constantan. The thermal gradient is established across these thermoelements by means of a heat source at the bottom surface and boiling water at the top surface. The dimensions and thermal conductivity of the elements are adjusted so that 1,000 watts will flow through the generating elements when the hot junctions are at a temperature not in excess of 350 degrees Centigrade, and the "cool" junctions are at the temperature of boiling water, or 100 degrees Centigrade. According to [redacted] the zinc antimonide- STAT constantan couples are capable of converting as much as 2.5 to 3 per cent of the thermal energy into electrical energy. Using 200 or more couples, it is possible by this means to produce approximately 5 volts at five amperes, or 25 watts.

The experimental program on this generator can be sub-divided into three areas:



MODEL OF THERMOELECTRIC GENERATOR ASSEMBLY

Figure 1

Area I: Heat-transfer studies on models without electrical output.

Particular interest is centered in the study of heat transfer from different kinds of heat sources, such as burners, fires, or hot plates to the hot junction terminal plate. Such studies are essential in order that the proposed geometry and temperatures may be proven to be adequate for the desired output.

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Area II: Study and adaptation to our needs of the [redacted] zinc-antimonide-constantan couple.

This includes the learning of the specialized techniques required for production and handling of zinc antimonide, and for affixing it to constantan. [redacted] STAT it is expected that investigation of this area can begin during the next quarter.

Area III: Problems concerned with combining the heat transfer studies of Area I with the materials studies of Area II into a finished thermoelectric generator.

Work of this sort can only take place after work on the other two areas has been well under way for some time.

Area I:

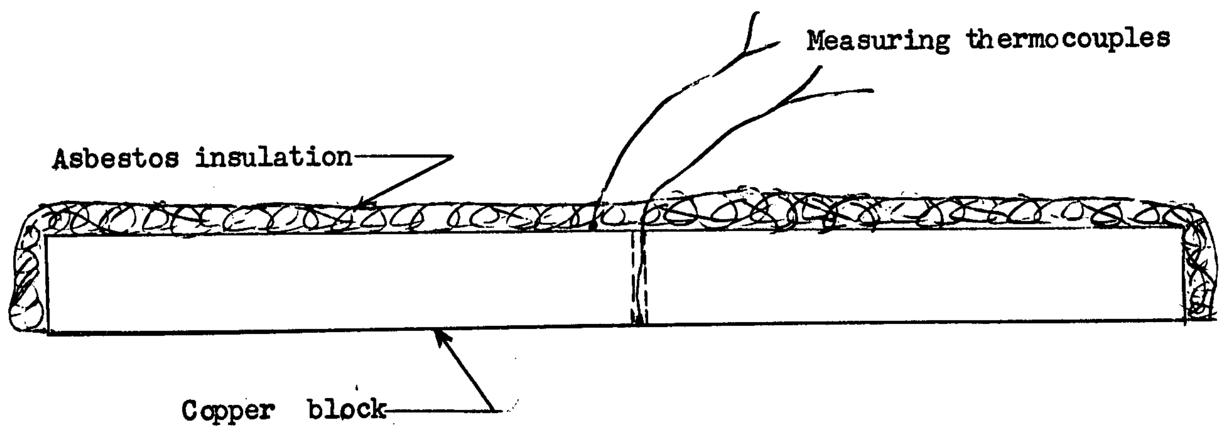
1. Heat Transfer Studies of Models of Complete Thermoelectric Generators.

A model was constructed of the finished thermoelectric generator, using two actual pie tins separated by a space of approximately 1/4 of an inch, similar to the sketch in Figure 1. The space between the pie tins was filled with glass, with a mixture of graphite and aluminum powder, and with a combination of this mixture and nickel shot. The purpose of using these diverse substances was to attempt to simulate the thermal characteristics of the zinc antimonide-constantan thermoelements in the finished products. The interior pan was filled with a measured quantity of water, and a burner was placed underneath the entire assembly. The time required to raise the water to the boiling point, as well as the time during which a measured quantity of water was evaporated from the array, was determined. It was then a relatively simple matter to calculate the heat required to raise the temperature of the water, as well as to boil that which disappeared; and, knowing the times for these processes, an estimate of the power during the boiling operation could be made. By means of a thermocouple affixed to the interior of the lower pan, it was also possible to determine the thermal gradient across the filling between the two pans.

It was found that the rates of heat transfer through the simulating fillings never approached 1000 watts, even though the temperature of the lower surface reached 600 degrees Centigrade. This plan of experiment was therefore abandoned. It was assumed that the powder nature of the filling material was not an adequate duplication of the solid thermoelements. The experimental program was, therefore, shifted to a more precise determination of the heat transferred from any heat source to a surface of a known temperature. This is described in the next subsection.

2. The Copper Calorimeter.

Two discs were constructed of metallic copper eight inches in diameter and one inch thick. The one face and the clindrical surface of these were covered with a heavy coat of asbestos to serve as thermal insulation. As shown in Figure 2, there was a thermocouple affixed to the lower surface and another to the upper surface of each of these discs. The thermal capacity of such copper pieces is 743 calories per degree Centigrade. In use, the heat source is placed on the uninsulated side of the copper calorimeter, and the temperature measured as a function of time. Occasional readings of the temperature at the upper surface of the calorimeter may be made by the use of the second thermocouple. The purpose of such a measurement is to assure a uniform temperature throughout



COPPER-BLOCK CALORIMETER

Figure 2

the major portion of the copper block. Experiment showed that at no time was the difference between the two thermocouples greater than five degrees Centigrade, a small percentage of the average temperature at the desired value of 350 degrees Centigrade.

The rate of heat transfer may be determined from the time and temperature data by plotting curves such as those shown in Figure 3. The upper curve shows an idealized heating curve for the copper block calorimeter. The slope of a tangent drawn at the temperature of interest gives the rate of increase of the temperature per unit time, which may then be converted to the number of calories per unit time. This figure may then be converted directly to the heat input in watts. The major advantage of using such a calorimeter is that the characteristics of heat transfer from any heat source to a copper surface, regardless of the temperature, may be determined merely by drawing a tangent at the temperature desired. The data obtained, therefore, are applicable even though another thermocouple system should be finally selected for use in the finished thermoelectric generator.

The copper block calorimeter is not without its drawbacks. There are losses of heat through the asbestos insulation which are not measured in the initial determination of heat input. To overcome this, both blocks were heated to approximately the same temperature, and the bare copper faces placed in juxtaposition. The temperature was then determined as a function of time during cooling. This cooling curve, shown in the lower portion of Figure 3, may be subjected to the same determination of slope as the heating curve, thereby producing a measure of the rate at which heat is lost through the thermal insulation at any temperature of interest. For example, at 350 degrees Centigrade, the rate of heat loss through the asbestos was found to be 134 watts.

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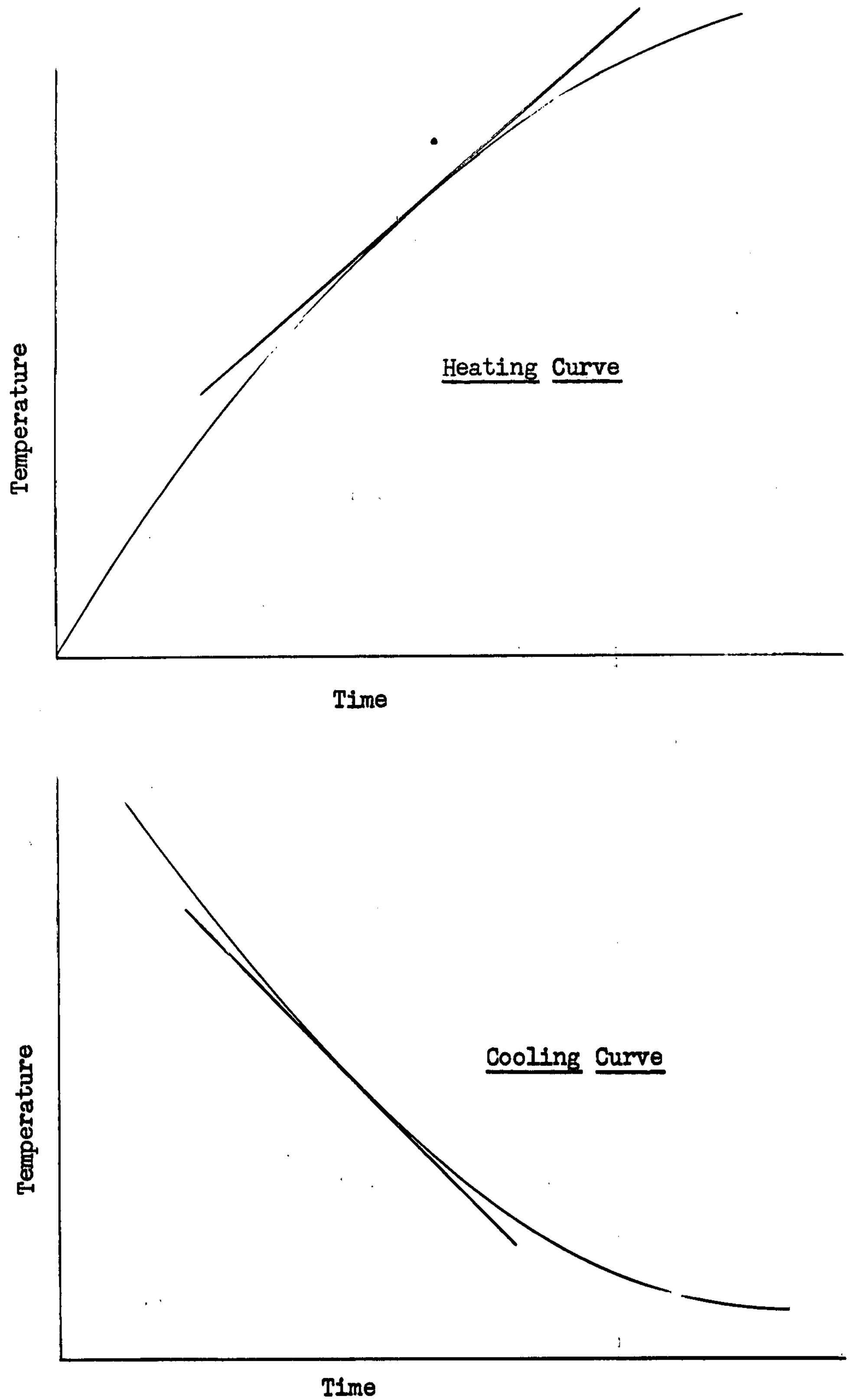
Heating Curve
Temperature
Time
Cooling Curve
Temperature
Time

Figure 3

This value has been added to the observed heat input values in the following table.

TABLE 1

Heat-Transferred to Copper Calorimeter from Various Heat Sources

SOURCE	CORRECTED HEAT INPUT TO CALORIMETER, WATTS
Laboratory gas burner	1163
Stove-type gas burner	757
Small gasoline burner	412

It will be observed that the only burner meeting the specifications in the above group is the one normally found only in chemical laboratories. A more efficient gas stove burner than the one employed will be used in an attempt to duplicate the results under more favorable conditions. A large gasoline stove has been ordered to ascertain if its use might appreciably increase the heat output. Other proposed heat sources for this part in the investigation are listed in the Section VI, under Program for the Next Period, Part B, Thermoelectric Generator Program.

Area II:

As stated above, the actual preparation of thermocouple materials awaits the arrival of a report promised by [redacted] STAT

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[redacted]

V. CONCLUSIONS

A. Study Program:

Although no specific conclusions can be reached on the merits of any particular system for production of electrical energy, the need has been demonstrated for more consultation with experts in the fields covered by this broad category. The possibility of production of a room temperature fuel cell operating from a hydrogen supply should be investigated. Also the possibility of utlizing information derived in Peltier cooling experiments for thermoelectric generators should be investigated.

B. Thermoelectric Generators:

Transfer of thermal energy from a heat source to the thermogenerator assembly must be investigated for a large number of heat sources. In the light of present results, it may be necessary to improve the ability of the generator to absorb heat from less-efficient sources of energy.

VI. PROGRAM FOR THE NEXT PERIOD

A. Study Program:

It is hoped that information which has been ordered from ASTIA will be obtained. A series of translations from Russian periodical literature in the field of thermoelectricity (also ordered) may prove of great interest. It is also planned that the staff will attend the meeting in October at Cleveland, Ohio, of the Electrochemical Society in order to learn of the latest developments in the battery field. It is hoped that contacts made at this meeting will enable the staff to have further fruitful discussions with experts in this area.

B. Thermoelectric Generator Program:

Other sources of heat such as wood fires, charcoal fires, more efficient gas burners, kerosene burners, and kitchen ranges will be employed in the heat transfer studies. A model of the thermoelectric generator which exactly duplicates the thermal properties of the thermoelements will be constructed and tested under several conditions.

[redacted] STAT

fabrication of thermoelements consisting of zinc antimonide and constantan will begin. The first phases of this process will include construction of equipment for production of the zinc antimonide itself. Studies of the means of handling this material and of its properties will be undertaken.

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